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2	1	Cog. Mgr. J.G. Kristofzski	<i>J.G. Kristofzski</i>	4/12/95							
2	1	QA T.C. Triple	<i>T.C. Triple</i>	4/13/95							
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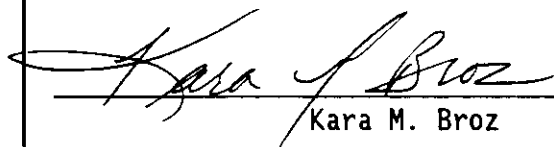
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Tank 241-B-104

Tank Characterization Plan

**Prepared for the U.S. Department of Energy
Office of Environmental Restoration
and Waste Management**

by

**Los Alamos Technical Associates
8633 Gage Boulevard
Kennewick, Washington 99336**

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TABLE OF CONTENTS

1.0	INTRODUCTION	1
2.0	DATA QUALITY OBJECTIVES APPLICABLE TO TANK 241-B-104	1
2.1	SAFETY SCREENING DATA QUALITY OBJECTIVES	1
2.2	PRETREATMENT DATA QUALITY OBJECTIVES	2
2.3	FUGITIVE VAPOR EMISSION DATA QUALITY OBJECTIVES	2
3.0	TANK AND WASTE INFORMATION	2
3.1	1995 TANK STATUS	2
3.2	TANK CONFIGURATION	3
3.3	AGE AND PROCESS HISTORY	3
3.4	EXPECTED TANK CONTENTS	5
4.0	TANK B-104 SCHEDULED SAMPLING EVENTS	6
5.0	REFERENCES	7

APPENDICES

A	SAMPLING AND ANALYSIS PLAN FOR PUSH CORE SAMPLING IN FISCAL YEAR 1995 . .	A-i
---	---	-----

LIST OF FIGURES

1:	Fill History for Tank 241-B-104	4
----	---	---

LIST OF TABLES

1:	Tank B-104 Solids Composite Inventory Estimate	5
2:	Integrated DQO Requirements	6

LIST OF ABBREVIATIONS

1C	first cycle waste
2C	second-cycle waste
B-104	Tank 241-B-104
B1SLTCK	242-B evaporator saltcake
DNFSB	Defense Nuclear Facilities Safety Board
DOE	Department of Energy
DQO	data quality objective
DST	double-shell tank
EB	evaporator bottoms waste
HEPA	high efficiency particulate
NCPLX	non-complexed waste
RCRA	Resource Conservation and Recovery Act
SAP	Sampling and Analysis Plan
SST	single-shell tank
TCP	Tank Characterization Plan
TOC	total organic carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company
WTR	wastewater

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1.0 INTRODUCTION

The Defense Nuclear Facilities Safety Board (DNFSB) has advised the Department of Energy (DOE) to concentrate the near-term sampling and analysis activities on identification and resolution of safety issues (Conway 1993). The data quality objective (DQO) process was chosen as a tool to be used to identify the sampling and analytical needs for the resolution of safety issues. As a result, a revision in the Federal Facility Agreement and Consent Order (Tri-Party Agreement) milestone M-44 has been made, which states that "A Tank Characterization Plan (TCP) will be developed for each double-shell tank (DST) and single-shell tank (SST) using the DQO process . . . Development of TCPs by the DQO process is intended to allow users (e.g., Hanford Facility user groups, regulators) to ensure their needs will be met and that resources are devoted to gaining only necessary information" (Ecology et al. 1994). This document satisfies that requirement for tank 241-B-104 (B-104) sampling activities.

2.0 DATA QUALITY OBJECTIVES APPLICABLE TO TANK 241-B-104

The sampling and analytical needs associated with the Hanford Site underground storage tanks on one or more of the four Watch Lists (ferrocyanide, organic, flammable gas, and high heat) and the safety screening of all 177 tanks have been identified through the DQO process. A DQO identifies the information needed by a program group concerned with safety issues, regulatory requirements, tank waste processing, or the transport of tank waste. The DQOs that have been completed and are applicable to tank B-104 are discussed in the following paragraphs.

2.1 SAFETY SCREENING DATA QUALITY OBJECTIVES

The *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) describes the sampling and analytical requirements that are used to screen waste tanks for unidentified safety issues. Both Watch List and non-Watch List tanks will be sampled and evaluated to classify waste tanks into one of three categories (SAFE, CONDITIONALLY SAFE, or UNSAFE). The safety screening DQO identifies the guidelines to determine to which classification a tank belongs based on analyses that indicate if certain measurements are within established parameters. The primary analytical requirements for the safety screening of a tank are energetics, total alpha activity, moisture content, and flammable gas concentration. If a specified parameter is exceeded, further analysis of a second set of properties and a possible Watch List classification would be warranted. A tank can be removed from a Watch List if it is classified as SAFE. As of January 1995, tank B-104 was classified as a non-Watch List tank.

The safety screening DQO requires that a vertical profile of the tank waste be obtained from at least two widely spaced risers. This vertical profile may be obtained using core, auger, or grab samples. These analyses shall be applied to all core samples, DST Resource Conservation and Recovery Act (RCRA) samples, and all auger samples, except those taken exclusively to assess the flammable gas crust burn issue.

2.2 PRETREATMENT DATA QUALITY OBJECTIVES

Interim Data Quality Objectives for Waste Pretreatment and Vitrification (Kupfer et al. 1994) addresses the characterization needs for the Pretreatment, High-Level Waste Disposal, and Low-Level Waste Disposal programs. These programs are responsible for developing long-term treatment and storage processes for the Hanford Site Waste. This effort will require comprehensive physical and chemical information from waste tank samples. The pretreatment process must be able to separate the waste into feed streams that satisfy the safety issues associated with the operating requirements for the low-level and high-level vitrification facilities.

2.3 FUGITIVE VAPOR EMISSION DATA QUALITY OBJECTIVES

The Tank Vapor Issue Resolution Program was initiated in 1992 to resolve the health and safety issues associated with the high level waste tanks at the Hanford site. The two main issues related to this program are 1) an insufficient understanding of reported exposures of tank farm personnel to unacceptable levels of noxious vapors and 2) the risks to worker health and safety can not be determined until the vapors in the waste tanks are well characterized. Westinghouse Hanford Company (WHC) standard safety practices dictate that any flammable components in the headspace of any Watch List tank must be determined and quantified before intrusive work can be conducted on these tanks. The DQO applicable to head space vapor sampling is *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994).

A nitrogen gas purge will be used to clear and cool the drill bit during rotary core sampling. This purge gas exhausts into the waste tank head space resulting in an uncontrolled release of pollutants. A portable modular unit has been developed to exhaust the tank head space during rotary core sampling. This modular unit will remove airborne particles through high efficiency particulate (HEPA) filters, but is not designed or equipped to treat or remove toxic vapors. It is equipped with instruments to monitor and alarm for total organic carbon (TOC) and ammonia vapors. The tank head space must be characterized to confirm that the modular unit can be safely started and to establish acceptable TOC and ammonia levels for safe operation. The applicable DQO for rotary core vapor sampling is the *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994).

3.0 TANK AND WASTE INFORMATION

This section summarizes the available historical information on tank B-104. Included are the age of the tank, process history, and the expected contents of the tank based on the latest information. The fill history information is available in *A History of the 200 Area Tank Farms* (Anderson 1990) and *Historical Tank Content Estimate for the Northeast Quadrant of the Hanford 200 East Area* (Brevick et al 1994).

3.1 1995 TANK STATUS

Tank B-104 is identified as a low-heat load non-Watch List tank, that is passively ventilated, and is categorized as sound with interim stabilization and

intrusion prevention completed. It entered service in August 1946 and as of December 31, 1994, it stored 1,404 kL (371 kgal) of non-complexed waste, which corresponds to a depth of 330 cm (130 inches). The waste is comprised of 3.9 kL (1 kgal) of supernatant; 230 kL (61 kgal) of saltcake; 340 kL (90 kgal) of unknown waste; and 829 kL (219 kgal) of sludge which includes 151 kL (40 kgal) of pumpable liquid remaining (Brevick et al. 1994). However, this contradicts with the current Hanlon document which, states that there are 261 kL (69 kgal) of saltcake, 3.9 kL (1 kgal) supernatant, and 1,140 kL (301 kgal) of sludge which includes 154 kL (47 kgal) of pumpable liquid remaining (Hanlon 1995).

The current maximum temperature reading from July 1993 is 66° F. Tank B-104 contains a single thermocouple tree with 12 thermocouple probes in riser 5. Specific thermocouple elevations are not available. Tank B-104 is a low-heat load tank and has a semiannual temperature monitoring requirement for January and July (Brevick 1994).

3.2 TANK CONFIGURATION

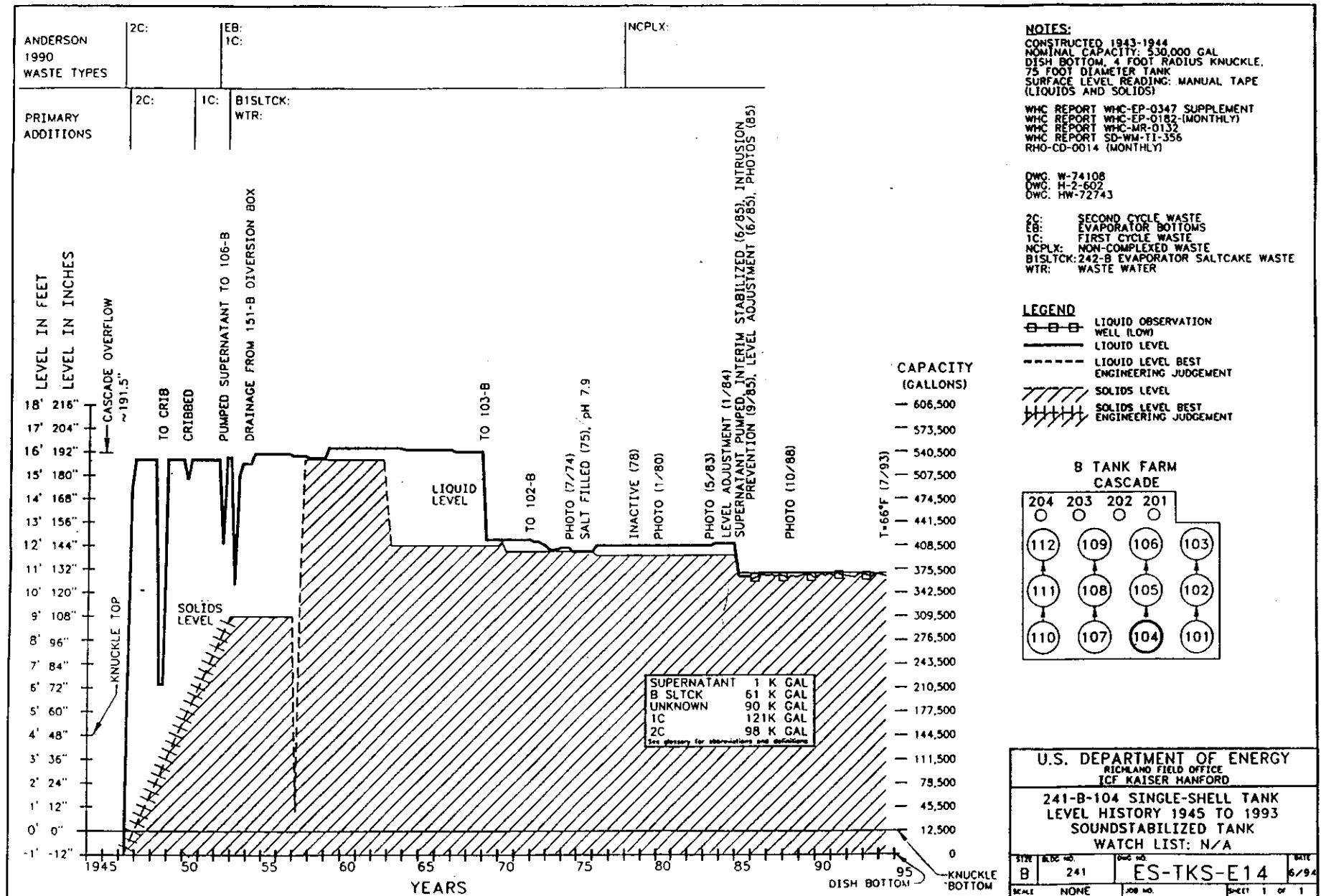
Tank B-104 was constructed between 1943 and 1944, and is located in the 200-East Area. The tank is a 100 series; 530,000 gal; 75 foot diameter single-shell tank. Built as a first generation tank, it was designed for nonboiling waste with a maximum fluid temperature of 220° F. Tank B-104 is the first in a cascade flow series consisting of tanks B-104, 241-B-105, and 241-B-106. A cascade flow system consists of tanks connected in a series by pipes. When the primary tank in the system became full, the waste would then flow to the secondary tanks in the system. Tank B-104 has 10 risers with two 12 inch risers (no. 2 and no. 3) available for use. Tank B-104 surface level is monitored quarterly with a manual tape through riser 8. The surface level for the past 3 years has remained steady and the readings range between 132 and 131.75 inches.

3.3 AGE AND PROCESS HISTORY

Activity began in tank B-104 when it was filled with second cycle waste between August 1946 and February 1947. During the fourth quarter of 1977 and the first quarter of 1978, a salt well was installed in the tank. Tank B-104 was declared inactive in 1978. Presently, the tank contains non-complexed waste.

In addition, a P-10 pump was installed in the third quarter of 1978 and a level adjustment was made in January 1984. In June of 1985, the tank was declared interim stabilized after it was saltwell-pumped. A level adjustment was made in June 1985, and intrusion prevention was completed in September 1985. One pH reading of 7.9 is listed on the level history in October 1975. Figure 1 shows the supernatant and solids waste levels of tank B-104 from 1946 to the present (Anderson 1990, Agnew 1994). Solids and supernatant levels were taken on a quarterly basis as part of the overall surveillance effort in the tank farms. Zero on the vertical scale is at the knuckle bottom of the tank and the dish bottom is 0.3 m (1 ft) below the knuckle bottom. The solids level in the tank is indicated by the shaded area and the supernatant level is indicated by the thick line above the shaded area (Brevick et al. 1994).

Figure 1: Fill History for Tank 241-B-104



3.4 EXPECTED TANK CONTENTS

Tank B-104 is expected to have two primary layer. A bottom sludge layer composed of first-cycle, second-cycle, and unknown waste, followed by a top layer of saltcake. The 1988 photographic montage of tank B-104 interior indicates a thin, bright yellow liquid covering part of the surface of an off-white salt-like waste material. The debris in the bottom of the picture contains: sludge measurement weights, old sample bottles, and some old level measurement tapes. There have been no changes in the tank which would affect the waste since these photographs were taken; therefore, the picture should be representative of the current tank contents. An estimated inventory based on historical sample and analysis data is shown in Table 1 (Brevick et al. 1994). This estimate is only based on the 1,400 kL (370 kgal) of sludge in the tank.

Table 1: Tank B-104 Solids Composite Inventory Estimate

Physical Properties			
Total Solid Waste	Mass = 1.44E+06 kg; Volume = 1,400 kL (370 kgal)		
Heat Load	4.76E-02 kW (1.62E+02 BTU/hr)		
Bulk Density	1.36 (g/cm ³)		
Void Fraction	0.62		
Water wt%	59.82		
TOC wt% C (wet)	0.00		
Chemical Constituents	moles/L	µg/g	kg
Na ⁺	6.67	1.13E+05	1.63E+05
Al ⁺³	0.14	2.83E+03	4.09E+03
Fe ⁺³ (total Fe)	0.22	8.95E+03	1.29E+04
Cr ⁺³	1.15E-02	4.37E+02	6.31E+02
Bi ⁺³	9.56E-02	1.47E+04	2.12E+04
Zr (as ZrO(OH) ₂)	1.26E-02	8.45E+02	1.22E+03
OH ⁻	1.24	1.55E+04	2.24E+04
NO ₃ ⁻	1.02	4.66E+04	6.72E+04
NO ₂ ⁻¹	5.77E-02	1.95E+03	2.81E+03
CO ₃ ²⁻	0.13	5.84E+03	8.43E+03
PO ₄ ³⁻	1.51	1.05E+05	1.52E+05
SO ₄ ²⁻	0.21	1.51E+04	2.17E+04
Si (as SiO ₃ ⁻²)	0.31	6.40E+03	9.24E+03
F ⁻¹	0.13	1.80E+03	2.60E+03
Cl ⁻¹	2.65E-03	69.02	99.61

Table 1: Tank B-104 Solids Composite Inventory Estimate

Radiological Constituents	C1/L	$\mu\text{Ci/g}$	C1
Pu		7.37E-02	1.77 (kg)
U	2.87E-02 (M)	5.02E+03 ($\mu\text{g/g}$)	7.24E+03 (kg)
Cs	2.12E-03	1.56	2.25E+03
Sr	5.19E-03	3.81	5.50E+03

4.0 TANK B-104 SCHEDULED SAMPLING EVENTS

Two sampling event for tank B-104 are currently scheduled: a core sample in and a vapor sample. No other sampling is scheduled through Fiscal Year 1997 (Stanton 1995). The core sampling shall be conducted in accordance with *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) and *Interim Data Quality Objectives for Waste Pretreatment and Vitrification* (Kupfer et al. 1994). The vapor sampling shall be conducted in accordance with *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994), and *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994). Sampling and analytical requirements from these DQOs are summarized in Table 2. A complete list of analytical requirements is given, as an appended attachment, in the appropriate Sampling and Analysis Plan (SAP).

An assessment has been performed, determining that acquisition and subsequent analysis of core samples from tank B-104 would provide valuable information. Several different technical and programmatic needs would be satisfied with this additional effort.

- (1) **Sampler Performance** - Field operations would gain experience with how the sampling system performs in a previously unknown environments, and changes/modifications to procedures can be tested and assessed (i.e. bit performance).
- (2) **Improve Quantitative Data Assessment** - More core composite samples together with segment (or sub-segment) level data provide additional robustness to the data sets, allowing additional questions to be answered. In addition, the stability and reliability of the statistical tests performed increases with the number of observations.
- (3) **Historical Evaluation** - This tank has a relatively straightforward process history. Taking the core samples and evaluating the historical model with the actual segment and composite level data provides a useful check on the assumptions and source terms used in the model.
- (4) **Spatial Variability Quantification** - The riser configuration and available risers for sampling B-104 are not well spaced for assessing this characteristic, since the risers are constrained to only opposite sides of the tank, with no access to the center. However, two cores taken from opposite sides of the tank will be sufficient to address general questions regarding lateral variability. The

historical information with regard to this tank indicates that there are several different waste layers in the tank. Statistical treatment of the data will demonstrate whether layering is evident and quantifiable.

(5) Tank Grouping - The waste types in tank B-104, especially the 1C and 2C wastes, contribute substantially to the overall waste volume in the tank farms. However, these waste types have been analyzed extensively from other tanks. The analysis provided from this tank will aid in evaluating the assumption that the waste types do not vary much in composition from tank to tank. There are also waste types in this tank that not very much is known about, B salt cake and a designated "unknown" layer (as described in the HTCE). The analysis of these materials will prove useful in broadening the knowledge about the wastes in the tanks in general. Furthermore, because of the complicated arrangement of the waste layers in this tank, information obtained about the spatial variability in this tank may be applicable as an upper bound to many tanks. Knowledge of the waste type compositions and uncertainties obtained from these tanks can be applied to other tanks that contain these materials.

Table 2: Integrated DQO Requirements

Sampling Event	Applicable DQO's	Sampling Requirements	Analytical Requirements
Push Core Sampling	<ul style="list-style-type: none"> ► Safety Screening DQO ► Pretreatment DQO 	Core samples from a minimum of 2 risers separated radially to the maximum extent possible	Energetics, Moisture, Total Alpha
Vapor Sampling	<ul style="list-style-type: none"> ► Generic In-Tank Vapor Issue ► Rotary Core Vapor Sampling DQO 	3 SUMMA® canisters 12 Triple Sorbent Traps 6 Sorbent Trap Systems	Gas Flammability Gas Toxicity -Organic Vapors -Permanent Gases

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APPENDIX A

**SAMPLING AND ANALYSIS PLAN FOR
PUSH CORE SAMPLING IN FISCAL YEAR
1995**

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TABLE OF CONTENTS FOR APPENDIX A

A1.0	TANK CHARACTERIZATION OBJECTIVES	A-1
A2.0	TANK STATUS AND SAMPLING INFORMATION	A-1
A2.1	TANK STATUS	A-1
A2.2	SAMPLING INFORMATION	A-1
A3.0	LABORATORY SAMPLE RECEIPT AND ANALYSIS INSTRUCTIONS	A-2
A3.1	TANK-SPECIFIC ANALYTICAL PROCEDURES	A-2
A3.2	INSUFFICIENT SEGMENT RECOVERY	A-5
A3.3	PRIORITIES OF REQUESTED ANALYSES	A-5
A4.0	SPECIFIC ANALYTE, QUALITY ASSURANCE, AND DATA CRITERIA	A-9
A4.1	SPECIFIC METHODS AND ANALYSES	A-9
A4.2	QUALITY ASSURANCE	A-9
A4.2.1	Laboratory Operations	A-9
A4.2.2	Sample Collection	A-9
A4.2.3	Sample Custody	A-10
A5.0	ORGANIZATION	A-13
A6.0	EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS	A-13
A6.1	EXCEPTIONS TO DQO REQUIREMENTS	A-13
A6.2	CLARIFICATIONS AND ASSUMPTIONS	A-14
A7.0	DELIVERABLES	A-15
A7.1	PROGRESS REPORTS	A-15
A7.2	FORMAT I REPORTING	A-15
A7.3	FORMAT III REPORTING	A-15
A8.0	CHANGE CONTROL	A-16
A9.0	REFERENCES	A-17

LIST OF TABLES FOR APPENDIX A

A-1:	Tank B-104 Chemical, Radiological, and Physical Analytical Requirements .	A-11
A-2:	Tank B-104 Project Key Personnel List	A-13

LIST OF FIGURES FOR APPENDIX A

A-1:	Solid Analysis Flowchart	A-6
A-2:	Liquid Analysis Flowchart	A-7
A-3:	Sample Analysis and Reporting Flowchart	A-8

LIST OF ABBREVIATIONS FOR APPENDIX A

ACL	Analytical Chemistry Laboratory
B-104	Tank 241-B-104
DOE	Department of Energy
DQO	data quality objective
DSC	differential scanning calorimetry
HHF	hydrostatic head fluid
IC	ion chromatography
ICP	inductively coupled plasma (atomic emission spectroscopy)
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
RSST	Reactive System Screening Tool
SAP	Sampling and Analysis Plan
SARP	Safety and Analysis Report Packaging
TCP	Tank Characterization Plan
TGA	thermogravimetric analysis
TOC	total organic carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

A1.0 TANK CHARACTERIZATION OBJECTIVES

This Sampling and Analysis Plan (SAP) will identify characterization objectives pertaining to sample collection, hot cell sample breakdown, and laboratory analytical evaluation and reporting requirements in accordance with the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) and *Interim Data Quality Objectives for Waste Pretreatment and Vitrification* (Kupfer et al. 1994). These Data Quality Objectives (DQO's) are described in the Tank Characterization Plan (TCP) for tank 241-B-104 (B-104). The pretreatment DQO, at the request of the Pretreatment Program, will have limited use in this SAP (refer to Section A6.1). This SAP will also identify procedures and requirements for collecting and characterizing samples from tank B-104 by the core sampling method.

A2.0 TANK STATUS AND SAMPLING INFORMATION

A2.1 TANK STATUS

Tank B-104 is identified as a low-heat load non-Watch List tank, that is passively ventilated, and is categorized as sound with interim stabilization and intrusion prevention completed. It entered service in August 1946 and as of December 31, 1994, it stored 1,404 kL (371 kgal) of non-complexed waste, which corresponds to a depth of 330 cm (130 inches). The waste is comprised of 3.9 kL (1 kgal) of supernatant; 230 kL (61 kgal) of saltcake; 340 kL (90 kgal) of unknown waste; and 829 kL (219 kgal) of sludge which includes 151 kL (40 kgal) of pumpable liquid remaining (Brevick et al. 1994). However, this contradicts with the current Hanlon document which, states that there are 261 kL (69 kgal) of saltcake, 3.9 kL (1 kgal) supernatant, and 1,140 kL (301 kgal) of sludge which includes 154 kL (47 kgal) of pumpable liquid remaining (Hanlon 1995).

The current maximum temperature reading from July 1993 is 66° F. Tank B-104 contains a single thermocouple tree with 12 thermocouple probes in riser 5. Specific thermocouple elevations are not available. Tank B-104 is a low-heat load tank and has a semiannual temperature monitoring requirement for January and July (Brevick 1994).

A2.2 SAMPLING INFORMATION

Tank B-104 is currently scheduled to be core sampled. Two core samples shall be collected from ~~risers X and X~~ of the tank. If a different riser is capable of meeting the intent of other requirements in the DQO, it may be used if the riser number is recorded and approved in writing in advance by the sampling cognizant engineer. Risers used may be recorded on a permanent data sheet, or recorded directly in a work package.

Based on current waste volume information, each of the core samples is expected to consist of seven segments. Segments 2 through 7 should be 48 cm (19 inches), and segment 1 should be 41 cm (16 inches). It should be noted that the sampling objective is to obtain a vertical profile of the waste; therefore, more or less segments may need to be taken depending on the accuracy of the current waste volume records. For detailed information regarding the sampling activities, refer to work package ES-95-166. This document contains operating procedures and the chain-of-custody records for this sampling event.

One field blank for this tank shall be obtained by filling a sampler with deionized water. This field blank is to accompany the samples to the laboratory hot cell. All collected samples shall be shipped to the laboratory according to procedure TO-080-090 ("Load/Transport Sample Cask(s)"). Core samples shall be transported to the laboratory within three calendar days of each segment's removal from the tank.

Occasionally, hydrostatic head fluid (HHF) with lithium bromide (LiBr) as a tracer may be used to aid in the collection of the core samples. If HHF is used, Sampling Operations must state this in the chain of custody form that accompanies the sample to the laboratory, and must also provide an HHF blank for the laboratory. The HHF blank shall consist of a container filled with HHF (with LiBr tracer) from the same batch of HHF used during the sampling. It shall be analyzed for Li (and Br if the Li notification limit is exceeded) in order to determine the concentration of the tracer at the time the core was taken. Only one HHF blank per tank is required. The HHF blank is required in addition to the field/trip blank (sampler filled with water).

A3.0 LABORATORY SAMPLE RECEIPT AND ANALYSIS INSTRUCTIONS

A3.1 TANK-SPECIFIC ANALYTICAL PROCEDURES

Flowcharts depicting the general safety screening sample breakdown and analysis scheme are presented in Figures A-1, A-2, and A-3. These steps are described in detail to provide the hot cell and laboratory chemists with guidance for the breakdown of the segments and may be altered as appropriate by the performing laboratory. Several analyses listed in Table A-1 require a 45 day reporting time, as noted. The 45-day reporting format, Format III, is explained in Section A7.3.

As a precautionary measure, the Safety and Analysis Report Packaging (SARP) in the work procedure TO-080-090 ("Load/Transport Sample Cask(s)") has been reviewed for any safety issues involved with transportation of core samples from tank B-104. For core samples from tank B-104, the shipping containers must be vented every 47 days to release retained gas.

Any decisions, observations, or deviations and justifications made to this work plan or during the sample breakdown shall be documented in writing. These decisions and observations shall also be reported in the data report. The reporting formats for analyses are contained in Table A-1.

- Step 1 Receive core samples at the laboratory in accordance with approved procedures.
- Step 2 Conduct the following on the material from each extruded segment:
- ▶ Perform a visual examination of the segment(s).
 - ▶ Record observations. This may include a sketch of the extruded core sample in addition to written documentation of pertinent descriptive information such as color, texture, homogeneity, and consistency.
 - ▶ Take color photographs and/or a videotape to visually document the extruded core segments.

Step 3 Is the segment 100% drainable liquid?

Yes: Proceed to Step 14

No: Proceed to Step 4

Step 4 Separate any drainable liquid from the solids. Measure and record the volume. Retain drainable liquids for further processing.

SOLIDS PATH

Step 5 Divide each extruded core segment into half-segments.

Step 6 Homogenize each half-segment using the appropriate, approved procedure.

Step 7 Will a homogenization test be performed?

Yes: Proceed to Step 8

No: Proceed to Step 9

NOTE: One homogenization test, at a minimum, should be used if a homogenization test is to be performed. Additional tests may be performed at the laboratory's discretion.

Step 8 Conduct the homogenization test by taking 1 to 2 g aliquots from widely separated locations of the homogenized subsample. Conduct the homogenization test in accordance with Bell (1993).

Step 9 Collect sufficient aliquots from each homogenized subsample to perform the appropriate preparations and analyses listed in Table A-1 in duplicate.

NOTE: If there is an insufficient amount of sample available in any subsample to perform all required analyses on the half-segment, notify the Characterization Program within one business day and follow the prioritization of analyses given in Section A3.3.

Step 10 Remove at least 20 mL and up to 40 mL of each homogenized subsample for the archive sample (Bratzel 1994).

Step 11 Combine half-segments proportional to the sludge recovery of the segment to build the solid composite of the core.

Step 12 Remove 100 mL of the solid composite as the Pretreatment solid composite archive (Bratzel 1994).

Step 13 Remove 125 mL of the solid composite for process development work (see Section A6.2).

NOTE: If insufficient sample material is available to provide an archive and a sample for process development of the sizes described, divide the material remaining after Step 11 into equal portions (i.e., equal-sized portions for archive and process development work).

LIQUIDS PATH

- Step 14 Closely inspect the liquid sample for the presence and approximate volume of any potential organic layers. Does the sample contain any immiscible (potentially organic) layers?
- Yes: Proceed to Step 15A
 No: Proceed to Step 16
- Step 15A Report any visually observed immiscible (potential organic) layer immediately by the early notification system (Section A7.2).
- Step 15B Separate and retain the potential organic layer for possible future analysis.
- NOTE: Steps 16 through 22 shall be performed on the remaining (probable aqueous) liquid layer only.
- Step 16 Filter the remaining liquid sample through a 0.45 micron filter.
- Step 17 Is there greater than 1 gram of solid on the filter?
- Yes: Proceed to Step 18
 No: Proceed to Step 19
- Step 18 Archive the solids for possible future analysis (Bratzel 1994).
- Step 19 Remove sufficient aliquots from the segment-level liquid sample to perform the appropriate analyses listed in Table A-1 in duplicate.
- Step 20 Archive at least 20 mL and up to 40 mL of the segment-level drainable liquid as the segment-level liquid archive (Bratzel 1994).
- Step 21 Combine the segment-level liquid proportional to the liquid recovery of the segment to build a liquid composite of the core.
- Step 22 Remove 100 mL of the liquid composite as the Pretreatment liquid composite archive (Bratzel 1994).

PRIMARY ANALYSIS PATH

- Step 23 Perform primary analyses as listed in Table A-1.
- Step 24 Compare the primary analysis data with notification limits.
- Step 25A Do the results exceed the notification limits (Table A-1)?
- Yes: Proceed to Step 25B.
 No: Proceed to Step 28.
- Step 25B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.

SECONDARY ANALYSIS PATH

- Step 26 Perform secondary analyses according to Table A-1.
- Step 27A Do the secondary analyses exceed the notification limits?
- Yes: Proceed to Step 27B
 No: Proceed to Step 28
- Step 27B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.
- Step 28 Report results as listed in Section A7.0.

A3.2 INSUFFICIENT SEGMENT RECOVERY

If the amount of material recovered from core samples taken from tank B-104 is insufficient to perform the analyses requested and to permit a minimum 20 mL archive per segment, the laboratory shall notify the Tank Cognizant Engineer, listed in Table A-2, within one working day. A prioritization of the analyses requested in this document is given in Section A3.3. Any analyses prescribed by this document, but not performed, shall be identified in the appropriate data report, with justification for non-performance.

A3.3 PRIORITIES OF REQUESTED ANALYSES

Confirmation of prioritization levels, or revision of sample breakdown procedures may be provided by the Characterization Program based upon the sample recovery, readily observable physical property distinctions within the sample, and the requested breakdown procedures as provided in Section A3.1. The priority of an analysis is specified by its designation as a primary or secondary analysis. Further prioritization will be determined by the program on a DQO basis.

Figure A-1: Solid Analysis Flowchart

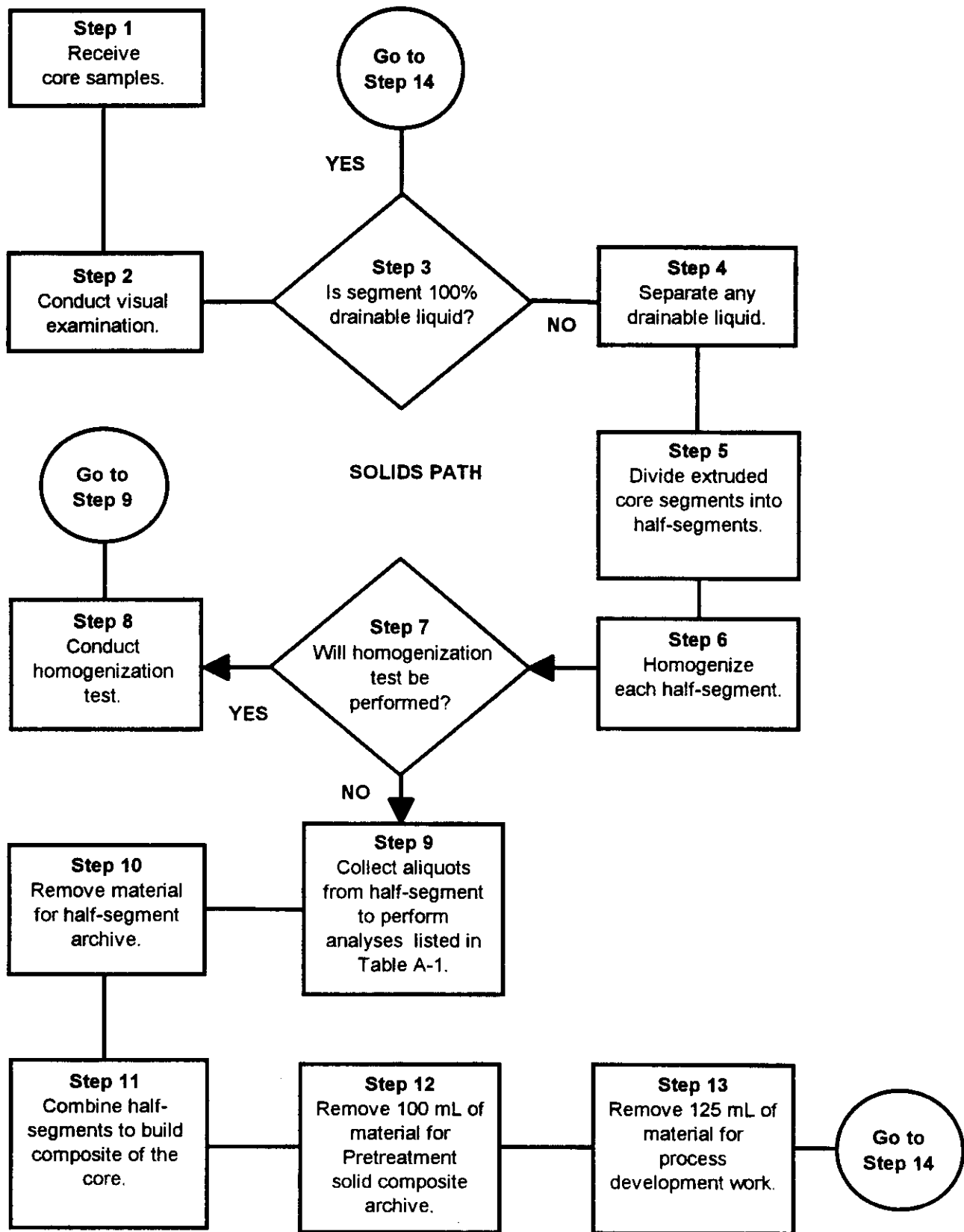


Figure A-2: Liquid Analysis Flowchart
LIQUIDS PATH

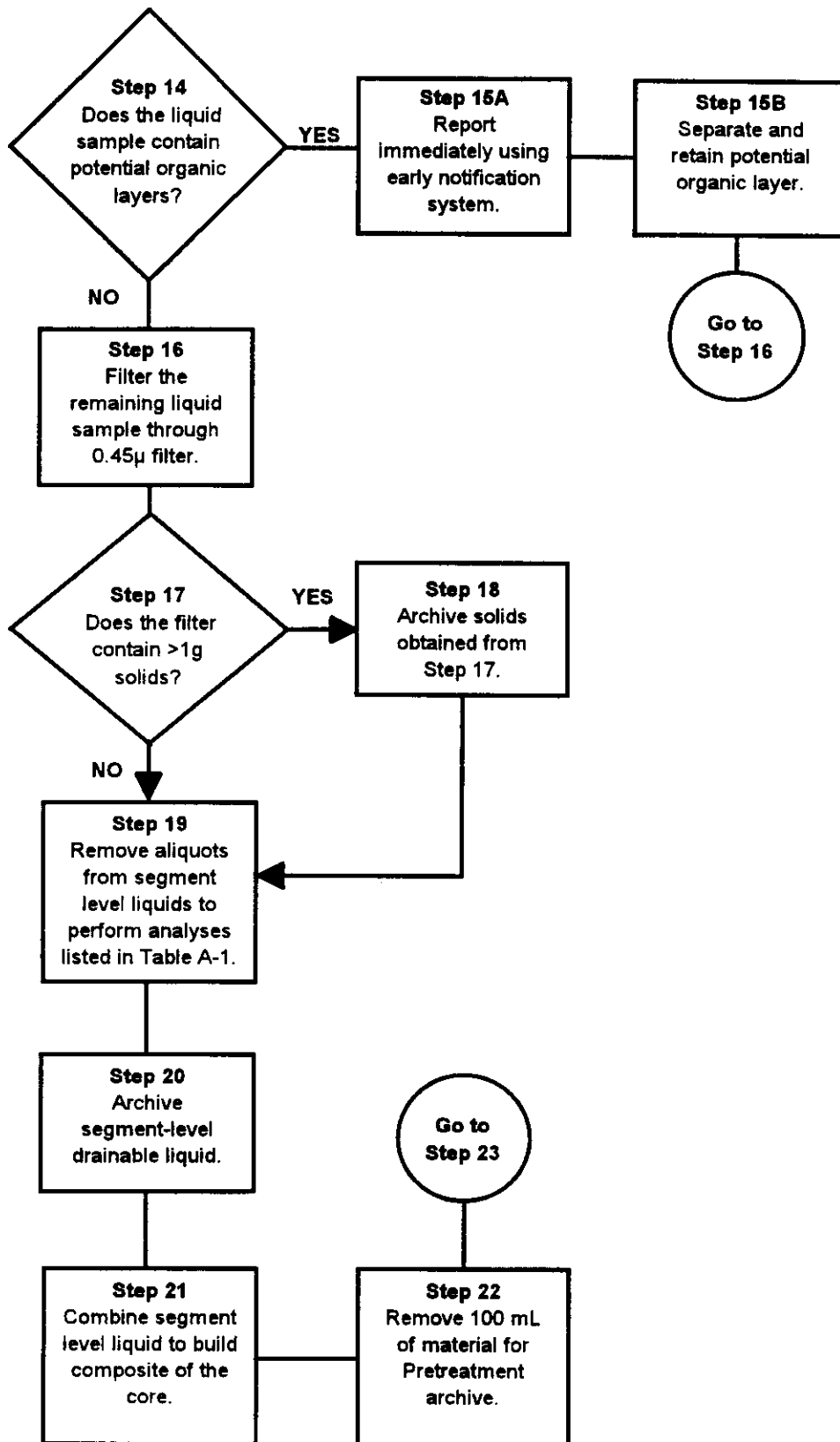
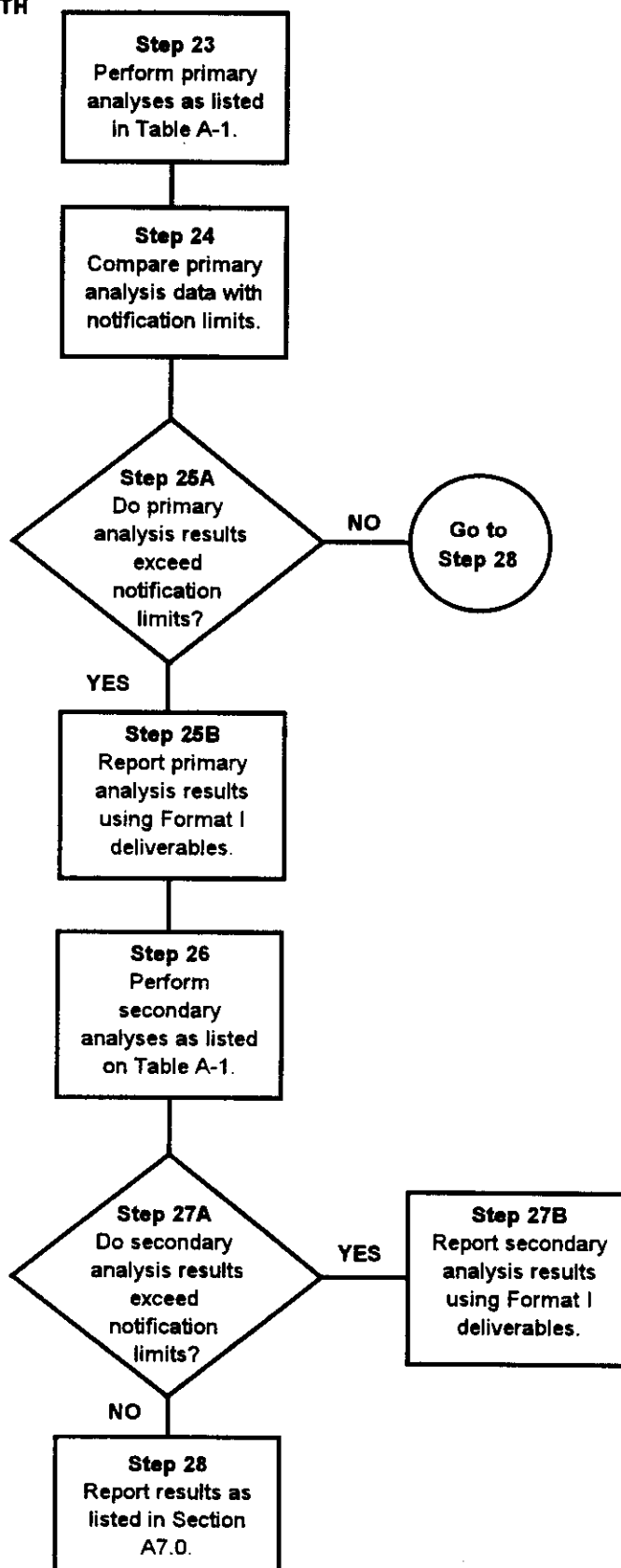


Figure A-3: Sample Analysis and Reporting Flowchart
ANALYSES PATH



A4.0 SPECIFIC ANALYTE, QUALITY ASSURANCE, AND DATA CRITERIA

A4.1 SPECIFIC METHODS AND ANALYSES

The analyses in Table A-1, to be performed on the tank B-104 core samples, are based on the safety screening DQO referenced in Section A1.0. The laboratory procedure numbers, which shall be used for the analyses, are included in the table.

A4.2 QUALITY ASSURANCE

A4.2.1 Laboratory Operations

The WHC 222-S Laboratory has a quality assurance program plan (Meznarich 1994) and a quality assurance project plan (Taylor 1993) that shall provide the primary direction for the quality assurance of analyzing the waste tank core samples at the WHC 222-S Laboratory. Additionally, the *Hanford Analytical Services Quality Assurance Plan* (DOE 1994), when implemented (currently scheduled for August 31, 1995), shall be used as quality assurance requirements.

Method-specific quality control such as calibrations and blanks are also found in the analytical procedures. Sample quality control (duplicates, spikes, standards) are identified in Table A-1. If no criteria are provided in Table A-1, the performing laboratory shall perform to its quality assurance plan(s).

A4.2.2 Sample Collection

Two core samples are to be taken from tank B-104 and shipped to the performing laboratory by Sampling Operations in accordance with work package ES-95-166. This work package shall also initiate the chain-of-custody for the samples. Approved procedure TO-080-090 ("Load/Transport Sample Cask(s)") is to be used during the sampling event. Samples shall be identified by a unique number before being shipped to the performing laboratory. The sampling team is responsible for documenting any problems and procedural changes affecting the validity of the sample in a field notebook. Sampling Operations shall enter this information in the comment section of the chain-of-custody form for addition to the data reports.

Sampling Operations should transport each segment collected to the performing laboratory within 1 working day of removing the segment from the tank, but must transport each segment within 3 calendar days. The field blank and HHF blank shall each count as a segment. Sampling Operations is responsible for verbally notifying the WHC 222-S Laboratory (373-2435) at least 24 hours in advance of an expected shipment.

A4.2.3 Sample Custody

The chain-of-custody form is initiated by the sampling team as described in work package ES-95-166. Core samples are shipped in a cask and sealed with a Waste Tank Sample Seal.

WASTE TANK SAMPLE SEAL	
Supervisor:	Sample No.:
Date of Sampling:	Time of Sampling:
Shipment No.:	Serial No.:

The sealed and labeled samples are shipped to the laboratory along with the chain-of-custody form. The receipt and control of samples in the WHC 222-S Laboratory are described in laboratory procedure LO-090-101.

Table A-1: Tank B-104 Chemical, Radiological, and Physical Analytical Requirements

SOLID ANALYSES															
Project Name		B-104 Push Mode Core Sample			COMMENTS							REPORTING LEVELS			
Plan Number		WHC-SD-WM-TP-349, REV. 0			Homogenization Test - Per Laboratory Discretion Field Blank - Required Hot Cell Blank - Not Required HHF Blank - Required							FORMAT I		Early Notify	
												FORMAT II		Process Control	
PROGRAM		PROGRAM CONTACTS										FORMAT III		Safety Screening	
A. Safety Screening		Safety Screening E. J. Lipke										FORMAT IV		Waste Management	
		TWRS R. D. Schreiber										FORMAT V		RCRA Compliance	
												FORMAT VI		Special	
PROGRAM	PRIMARY ANALYSES			SAMPLE ¹	PREP ²	QUALITY CONTROL ³						CRITERIA			FOR-MAT
	METHOD	ANAL.	WHC PROCEDURE	½ SEG SLDG		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴	
A	DSC	Energy	LA-514-113	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	J/g ⁵	> 481	unknown	I, III
A	TGA	% H ₂ O	LA-560-112	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	wt%	< 17	unknown	I, III
A	Alpha	Total Alpha	LA-508-101	X	f or a	ea smpl	1/mtrx	ea PB	ea AB	±10	90-110	µCi/g	> 41	unknown	I, III
A	ICP ¹¹	Li	LA-505-151	X ¹¹	f or a	ea smpl	see 7	ea PB	ea AB	±10	90-110	µg/g	> 100	unknown	I, III
PROGRAM	SECONDARY ANALYSES			SAMPLE ¹	PREP ²	QUALITY CONTROL ³						CRITERIA			FOR-MAT
	METHOD	ANAL.	WHC PROCEDURE	½ SEG SLDG		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴	
A	Distillation ⁸	CN	LA-695-102	X	d	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg/g	> 39,000	unknown	I, III
A	Sep. & α counting ⁹	Pu-239/240	LA-503-156	X	f	ea smpl	1/mtrx ⁸	ea PB	ea AB	±10	90-110	µCi/g	> 41	unknown	I, III
A	ICP ⁹	Fe	LA-505-151	X	f or a	ea smpl	see 7	ea PB	ea AB	±10	90-110	µg/g	none	8,950	III
A	ICP ⁹	Mn	LA-505-151	X	f or a	ea smpl	see 7	ea PB	ea AB	±10	90-110	µg/g	none	unknown	III
A	ICP ⁹	U	LA-505-151	X	f or a	ea smpl	see 7	ea PB	ea AB	±10	90-110	µg/g	none	5,000	III
A	IC ¹⁰	Br	LA-533-105	X	w	ea smpl	1/mtrx	ea PB	ea AB	±10	90-110	µg/g	> 1200	unknown	I, III
A	RSST ⁸	Energy	see 8 below	X	d	N/A	N/A	N/A	ea AB	±10	90-110	J/g ⁵	> 481	unknown	I, III
A	Hot Persulfate ⁸	TOC	LA-342-100	X	d	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg C/g	> 30,000	unknown	I, III

¹ ½ SEG SLDG-½ segment, sludge² d-direct, f-fusion, a-acid, w-water³ PR-precision, AC-accuracy, ea-each, smpl-sample, DUP-duplicate, SPK/MSD-spike and matrix spike duplicate, AB-analytical batch, PB-preparation blank, N/A-not applicable, mtrx-matrix⁴ Units for notification limits and expected range are those listed in the "units" column.⁵ Dry weight basis.⁶ Tracer or carrier may be used in place of a spike and results corrected for recovery.⁷ Either serial dilutions or matrix spikes will be performed.⁸ These analyses required if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.⁹ Performed only if total alpha exceeds notification limit.¹⁰ Performed only if Li exceeds notification limit.¹¹ If the chain of custody form indicates that HHF fluid with LiBr tracer was used to obtain the segment, Li analysis is to be performed on that segment.

Table A-1: Tank B-104 Chemical, Radiological, and Physical Analytical Requirements

LIQUID ANALYSES															
Project Name		B-104 Push Mode Core Sample			COMMENTS							REPORTING LEVELS			
Plan Number		WHC-SD-WM-TP-349 REV. 0			Homogenization Test - Per Laboratory Discretion Field Blank - Required Hot Cell Blank - Not Required HHF Blank - Required							FORMAT I		Early Notify	
												FORMAT II		Process Control	
PROGRAM		PROGRAM CONTACTS										FORMAT III		Safety Screening	
A. Safety Screening		Safety Screening		E. J. Lipke								FORMAT IV		Waste Management	
		TWRS		R. D. Schreiber								FORMAT V		RCRA Compliance	
												FORMAT VI		Special	
PROGRAM	PRIMARY ANALYSES			SAMPLE ¹	PREP ²	QUALITY CONTROL ³						CRITERIA			FOR-MAT
	METHOD	ANAL.	WHC PROCEDURE	FB & S-LEV LIQ		DUP	SPK/ MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴	
A	DSC	Energy	LA-514-113	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	J/g ⁵	> 481	unknown	I, III
A	TGA	% H ₂ O	LA-560-112	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	wt%	< 17	unknown	I, III
A	ICP ¹¹	Li	LA-505-151	X ¹¹	d ⁶	ea smpl	see 7	ea AB	ea AB	±10	90-110	µg/mL	> 100 ¹⁰	unknown	I, III
A	Visual	Organic Layer	LA-519-151	X	d	N/A	N/A	N/A	N/A	N/A	N/A		presence	unknown	I, III
PROGRAM	SECONDARY ANALYSES			SAMPLE ¹	PREP ²	QUALITY CONTROL ³						CRITERIA			FOR-MAT
	METHOD	ANAL.	WHC PROCEDURE	FB & S-LEV LIQ		DUP	SPK/ MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴	
A	Distillation ⁸	CN	LA-695-102	X	d ⁶	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg/mL	> 39,000 ¹⁰	unknown	I, III
A	IC ⁹	Br	LA-533-105	X	d ⁶	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg/mL	> 1,200 ¹⁰	unknown	I, III
A	RSST ⁸	Energy	see 8 below	X	d	N/A	N/A	N/A	ea AB	±10	90-110	J/g ⁵	> 481	unknown	I, III
A	Hot Persulfate ⁸	TOC	LA-342-100	X	d ⁶	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg C/mL	> 30,000 ¹⁰	unknown	I, III

¹S-LEV LIQ-liquid taken from the segment level, FB-field blank²d-direct, f-fusion, a-acid, w-water³PR-precision, AC-accuracy, ea-each, smpl-sample, DUP-duplicate, SPK/MSD-spike and matrix spike duplicate, AB-analytical batch, PB-preparation blank, N/A-not applicable, mtrx-matrix⁴Units for notification limits and expected range are those listed in the "units" column.⁵Dry weight basis.⁶Direct liquid samples may be diluted in acid or water to adjust to proper sample size and/or pH.⁷Either serial dilutions or matrix spikes will be performed.⁸These analyses required if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.⁹Performed only if Li exceeds notification limit.¹⁰Converted from µg/g limit assuming a liquid density of 1.0 g/mL.¹¹If the chain of custody form indicates that HHF fluid with LiBr tracer was used to obtain the segment, Li analysis is to be performed on that segment.

A5.0 ORGANIZATION

The organization and responsibility of key personnel involved with this tank B-104 characterization project are listed in Table A-2.

Table A-2: Tank B-104 Project Key Personnel List

Individual	Organization	Responsibility
J Jo	TWRS Characterization Plans and Reports	Tank B-104 Tank Characterization Plan Cognizant Engineer
E. J. Lipke	WHC Characterization Program	Safety Screening Point of Contact
M. J. Kupfer	Process Systems Engineering	Pretreatment Point of Contact
East Tank Farm Operations Shift Manager	Tank Farm Operations	200 East Tank Farm Point of Contact if Action Limit is Exceeded (373-2689)

A6.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS**A6.1 EXCEPTIONS TO DQO REQUIREMENTS**

In the safety screening DQO, it is specified that cyanide analyses are to be run on a quarter-segment level and that the notification limit for the DSC analysis is 125 cal/g (523 J/g). The revised ferrocyanide DQO (Meacham et al. 1994) has changed the requirements such that the cyanide analysis is now to be run on a half-segment level and the DSC notification limit is 115 cal/g (dry weight basis). The next revision to the safety screening DQO will incorporate this change. Therefore, although this Sampling and Analysis Plan uses the current safety screening DQO, it specifies that cyanide is to be run on a half-segment basis and that notification shall be made if the DSC value exceeds 481 J/g dry weight basis (115 cal/g).

In the pretreatment DQO, a wide array of analyses has been requested. However, it has been determined by the Pretreatment Program that all of these analyses are not necessary for these samples. If necessary, the Pretreatment Program will personally contact the laboratory to run analyses on the archived composite samples. Therefore, the Pretreatment Program has directed that only a 125 mL composite solid sample for process development, and a 100 mL composite sample for archive shall be obtained from this sampling event (Slankas 1994).

A6.2 CLARIFICATIONS AND ASSUMPTIONS

A number of clarifications and assumptions relating to the notification limits or decision thresholds identified in the applicable DQO efforts need to be made with respect to the analyses in Table A-1. Each of these issues are discussed below.

- Any exotherm (in J/g or cal/g) determined by DSC must be reported on a dry weight basis as shown in equation (1) using the weight percent water determined from thermogravimetric analysis.

$$\text{Exotherm (dry wt)} = \frac{[\text{exotherm (wet wt)} \times 100]}{(100 - \% \text{ water})} \quad (1)$$

NOTE: If there is greater than 90 percent water in a sample, converting to a dry weight basis may lead to a large error in the DSC value. However, the conversion is still required.

- The safety screening DQO (Babad and Redus 1994) requires that additional analyses be performed if total alpha activity measures greater than 1 g/L. Total alpha is measured in $\mu\text{Ci/g}$ rather than g/L. To convert the notification limit for total alpha into a number more readily usable by the laboratory, it was assumed that all alpha decay originates from Pu-239. The notification limit may then be calculated as shown in equation (2):

$$\left(\frac{1 \text{ g}}{\text{L}}\right) \left(\frac{1 \text{ L}}{10^3 \text{ mL}}\right) \left(\frac{1 \text{ mL}}{\text{density g}}\right) \left(\frac{0.0615 \text{ Ci}}{1 \text{ g}}\right) \left(\frac{10^6 \mu\text{Ci}}{1 \text{ Ci}}\right) = \frac{61.5 \mu\text{Ci}}{\text{density g}} \quad (2)$$

NOTE: If a density of 1.5 g/mL is assumed for solid material, the notification limit becomes 41 $\mu\text{Ci/g}$.

- The safety screening DQO, upon which some of the analyses in Table A-1 are based, does not sufficiently address the analyses of the field blank or any drainable liquid present. In order to characterize the tank waste adequately, all analyses performed on the solids for the safety screening DQO, with the exception of total alpha analyses, shall also be performed on any drainable liquids. To adequately determine if contamination of the sample material has occurred, the field blank shall be analyzed for those primary analyses done on the segment-level liquid.
- The Pretreatment Program has requested 125 mL of the solid composite material for process development work. A test plan (Lumetta and Rapko 1994; Temer 1994) will be used to guide this process development work. Since the Characterization Program is responsible for the taking of tank samples, the Characterization Program will need to approve the test plan. This approval will not only ensure that the DQO process has been used in the generation of the test plan and that there is justification for the samples, but also that the facility receiving the samples is in an adequate position to handle radioactive material. At such time that the test plan is approved by the Characterization Program, the Characterization Program will direct the performing laboratory, via a letter of instruction, to allow shipment of the sample material to the Process Chemistry section of PNL.

A7.0 DELIVERABLES

All analyses of tank B-104 waste material shall be reported as Format I and/or III as indicated in Table A-1. Additional information regarding reporting formats is given in "Revised Interim Tank Characterization Plan Guidance" (Schreiber 1994a).

A7.1 PROGRESS REPORTS

Each laboratory performing analyses on tank B-104 waste material from this core sampling project shall provide monthly status reports to the Characterization Program. This report shall contain 1) a summary of the activities on the analysis of tank B-104, 2) preliminary results to the program, and 3) schedule and cost information on a DQO basis.

Monthly and accumulative costs will be compared to the base as part of the progress report. Monthly variances greater than 10% or \$10,000, and accumulative variances greater than \$50,000 from the estimated costs or schedule must be explained in the report. Cost reporting shall consist of the following:

1. budgeted cost of work scheduled
2. monthly cost (actual cost of work performed)
3. year-to-date costs (actual cost of work performed)

Schedule reporting shall consist of the following:

1. monthly schedule
2. year-to-date schedule

A7.2 FORMAT I REPORTING

Table A-1 contains the notification limits for each analyte. Any results exceeding their notification limits shall be reported by calling the East Tank Farm Operations Shift Manager at 373-2689 and the Characterization Program (Schreiber 1994b). This verbal notification must be followed within 1 working day by written communication, documenting the observations, to Characterization Plan and Reports, Characterization Program Office, Safety Screening Representative, and Process Control (Schreiber 1995). Additional analyses for verification purposes may be contracted between the performing laboratory and the contacts above by a revision to this document, or by a letter of instruction.

A7.3 FORMAT III REPORTING

A Format III report, containing the results of the primary safety screening analyses shall be issued to the Safety Screening Representative, Characterization Plan and Reports, Characterization Program Office, Los Alamos Technical Associates, Tank Characterization Resource Center Process Control, and the Tank Characterization Database representative (Schreiber 1995) within 45 days of receipt of the last segment of the last core sample at the laboratory loading dock. The DSC and TGA scans have been requested due to the interpretive nature of the analysis. If analyses for the safety screening secondary analytes are required, these results

shall be provided within 90 days of receipt of the last segment of the last core sample at the laboratory loading dock. No calibration data are requested for these reports. Detailed information regarding the contents of this reporting format are given in Schreiber (1994a).

A8.0 CHANGE CONTROL

Under certain circumstances, it may become necessary for the performing laboratory to make decisions concerning a sample without review of the data by the customer or the Characterization Program. These changes shall be documented through the use of internal characterization change notices or analytical deviation reports for minor low-impact changes and documented in applicable laboratory records. All significant changes (such as changes in scope) shall be documented by Characterization Plans and Reports via an Engineering Change Notice to this Tank Characterization Plan. All changes shall also be clearly documented in the final data package.

Additional analysis of sample material from this characterization project at the request of the Characterization Program shall be performed according to a revision of this Tank Characterization Plan.

A9.0 REFERENCES

- Babad, H. and K. S. Redus, 1994, *Tank Safety Screening Data Quality Objective*, WHC-SD-WM-SP-004, Rev 0, Westinghouse Hanford Company, Richland, Washington.
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- DOE, 1994, *Hanford Analytical Services Quality Assurance Plan*, DOE/RL-94-55, Rev. 0, U. S. Department of Energy, Richland Field Office, Richland, Washington.
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